Thermal Magnetic Noise Spectra of Nanoparticle Ensembles

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Aim: Characterization of Magnetic Nanoparticles for Biomedical Applications

BIOMEDIAL APPPLICATIONS

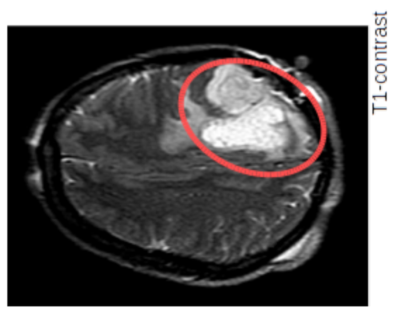
Magnetic nanoparticles enjoy a lot of interest due to their appealing properties for **biomedical applications**.
For instance, when exposed to an alternating magnetic field, they generate heat which can be used in the destruction of cancer cells (**magnetic hyperthermia**).
Furthermore, when equipped with a suitable coating, they can be ideal **drug carriers** or **disease detectors.** Finally, the combination of the small sizes enabling virtually full body detection and the large magnetic moment enabling non-invasive detection, makes them excellent candidates for use in **imaging applications**.
However, for these applications to work reliably, the magnetic properties of the nanoparticles should be well-known.

CHARACTERIZATION METHODS

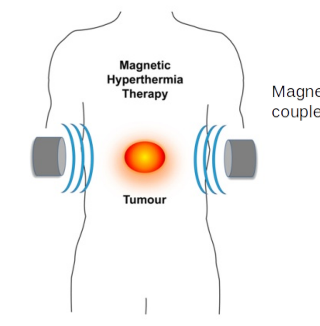
Many techniques are capable of investigating the magnetic moment of an ensemble of nanoparticles. Most of these measurements require the use of an external magnetic field.
Examples are static magnetization measurements such as **room temperature magnetization curves** or dynamic measurements such as **AC susceptometry** or **magnetic particle spectroscopy**.
Alternatively, one can investigate the relaxation of the magnetic moment of the nanoparticle sample after the magnetic field is switched off (**magnetorelaxometry (MRX)**).

NEW CHARACTERIZATION METHOD: THERMAL MAGNETIC NOISE SPECTRA (TMNS)

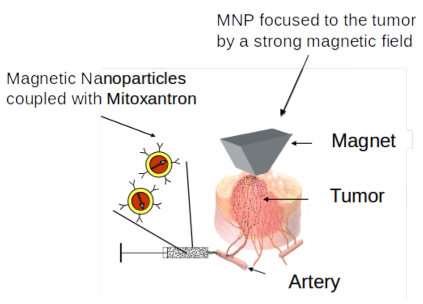
A **novel approach**, in the absence of an external field, is to measure the **thermal magnetic noise spectrum (TMNS)** resulting from the thermal switching of the nanoparticles.
On **this poster**, we present the measured noise spectrum of several magnetic nanoparticle samples.
We present a model to estimate the size distribution of the particles from the noise spectrum and compare it to those from magnetorelaxometry data of the same samples.



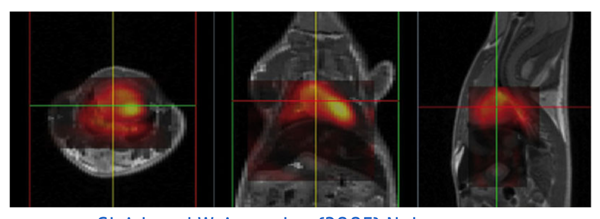
Taupitz et al. (1993) Acta Radiol.



Andrade et al. (2011) Intech



Alexiou et al. (2011) JMMM



Gleich and Weizenecker (2005) Nature

Theoretical Background

FLUCTUATION PROCESSES

The fluctuations of the magnetic moment of nanoparticles are the result of **two distinct processes**:
1) the spatial rotation of the nanoparticle as a whole and 2) thermal switching in which only the magnetic moment changes direction.
Both processes give rise to **characteristic fluctuation rates** $\nu_\mathrm{B} = \frac{k_\mathrm{B}T}{3\eta V_\mathrm{h}}$ and $\nu_\mathrm{N} = \nu_0 \exp\left(\frac{-KV_\mathrm{c}}{k_\mathrm{B}T}\right)$ which depend on the size, the material parameters and the environment of the particles. In these equations, V_c and V_h are the core and hydrodynamic diameters, respectively; K denotes the anisotropy constant, k_B is the Boltzmann constant, T is the temperature, eta is the viscosity, and ν_0 is an attempt frequency of 0.1 GHz. When both processes are present, the fluctuations can be characterized by an effective fluctuation rate $\nu_\mathrm{eff} = \nu_\mathrm{N} + \nu_\mathrm{B}$.

MAGNETORELAXOMETRY

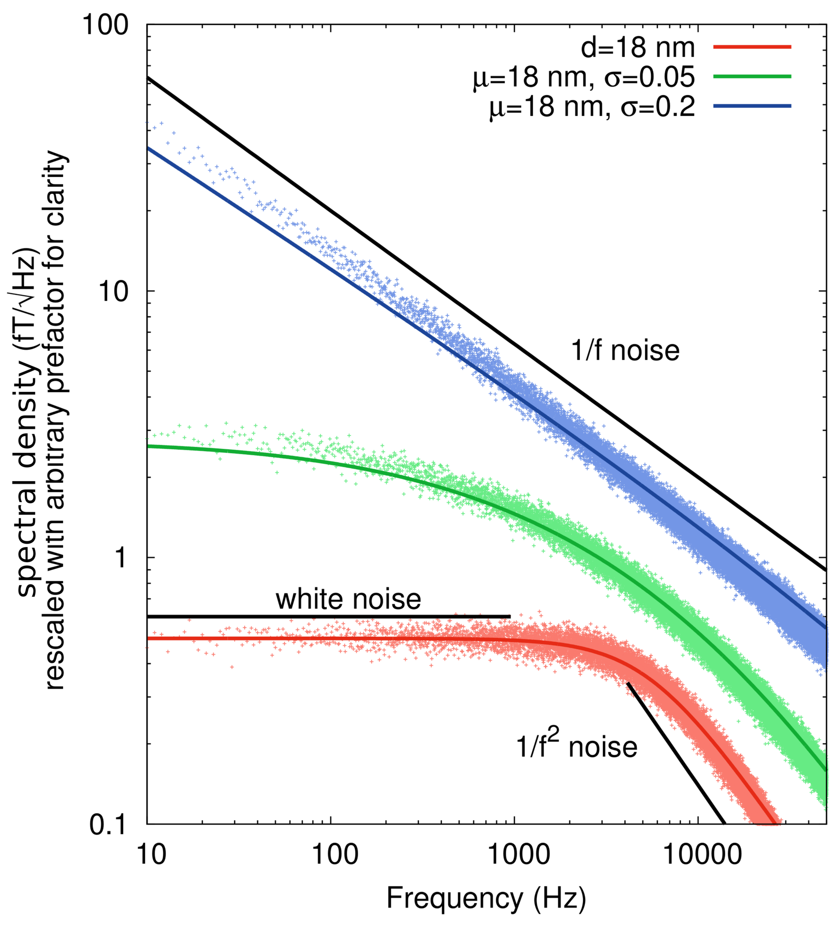
This fluctuation rate can also be interpreted as the inverse of the **relaxation time** $\tau_\mathrm{eff} = \frac{1}{2\nu_\mathrm{eff}}$ with which a sample of nanoparticles relaxes again after it has been magnetized in an external field. In an MRX experiment, the relaxing magnetic moment is recorded and interpreted with the help of $M(t) = \int_V M_0 V \exp\left(-\frac{t}{\tau_\mathrm{eff}(V)}\right) P(V) dV$ where P(V) denotes the size distribution.

NOISE POWER SPECTRUM

It is well-known that the noise power spectrum from the random switching of a magnetic moment has a **Lorentzian shape** $S(f) = \int_0^\infty \frac{g(\nu)\nu/2}{\nu^2 + (\pi f)^2} d\nu$, with $g(\nu) = P(\nu_\mathrm{eff}(V))$. The noise spectrum of a monodisperse ensemble of magnetic nanoparticles also has this shape. It is characterized by a flat **white noise part up to the cutoff frequency , after which the noise power rapidly decreases as 1/f²** .

SIZE DISTRIBUTION

The nanoparticles' size distribution impacts the noise spectrum. Both the noise spectrum and the MRX data of the samples are determined by the size dependent rates, so the particle sizes can be estimated by fitting the experimental data. To this end, typically the **lognormal diameter distribution** is assumed: $P(D) = \frac{1}{\sqrt{2\pi}\sigma D} \exp\left(-\frac{\ln^2(D/\mu)}{2\sigma^2}\right)$



Simulated noise spectra of three different size distributions. This figure proves that the noise spectra are well described by a superposition of Lorentzians and illustrates the transition from 1/f² noise to 1/f noise for broader distributions The light-colored datapoints are generated with Vinamax, a software package which numerically solves the Landau-Lifshitz equation , describing the magnetic dynamics. The full darker lines depict the theoretically expected spectra. The red curve depicts the spectrum of a monodisperse ensemble with all particle diameters equal to 18 nm, while the green and blue curves correspond to lognormal size distributions with μ=8 nm and σ = 0,05 and 0.2, respectively.

Methods and Measurement Data

SETUP

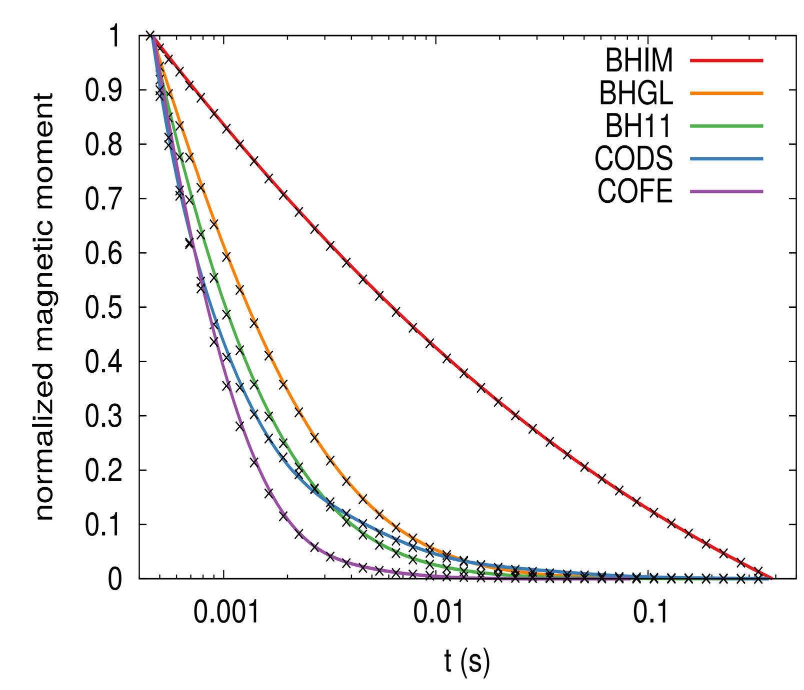
Noise and MRX measurements of 5 different samples were performed in the 8-layered **magnetically shielded room** at Physikalisch-Technische Bundesanstalt (PTB) in Berlin. **A single channel MRX system** was used for both the noise measurements and MRX measurements. It contains a **low Tc SQUID** in a dewar. The sample is placed outside the dewar in a 150 μl cuvette, 12 mm below the SQUID. MRX measurements at T = 295 K are performed by applying a magnetic field of 1 mT to the sample for 1 s. After a dead time of 200 μs, the MRX signal is recorded for 0.5 s. The coil system generating the magnetic field for the MRX measurements is removed during noise measurements to avoid the related background noise. The sensor signal is guided to a spectrum analyzer which records the noise spectra of the samples in units of fT/ Hz$^{1/2}$

MEASUREMENTS

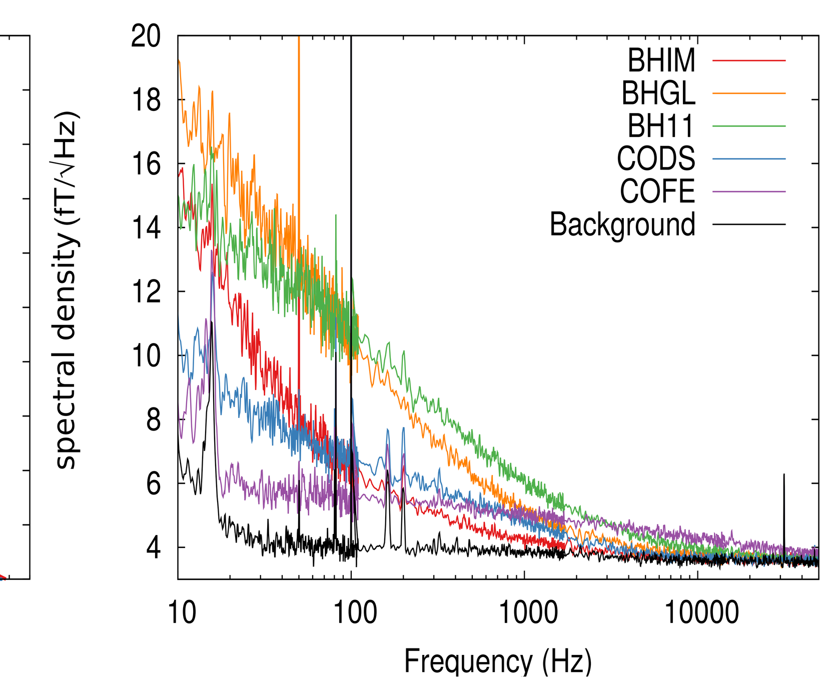
The measurements were performed in 4 frequency windows (10 Hz–110 Hz, 100 Hz–1.7 kHz, 1.6 kHz–14.4 kHz, and 12.8 kHz–50 kHz), which were logarithmically divided into 800 points. For practical reasons, only 50 averages were taken in the first window, while 500 averages were taken in the other windows. Using the same setting, the background noise spectrum was recorded using an empty sample holder.

SAMPLES

The samples used in this study are iron oxide particles dispersed in water from Berlin Heart GmbH with an iron concentration of 55.7 mg/ml which were 1:1 diluted with water **[BH11]**, 1:1 diluted with glycerol **[BHGL]** and immobilized in gypsum **[BHIM]**. We also used a cobalt ferrite sample (SiMAG/CF-Carboxyl) acquired from Chemicell GmbH **[COFE]** and cobalt ferrite nanoparticles with a silica shell **[CODS]**. For the latter one, the magnetic core was prepared via a co-precipitation method and afterwards covered via a silica shell by a modified Stoeber process.



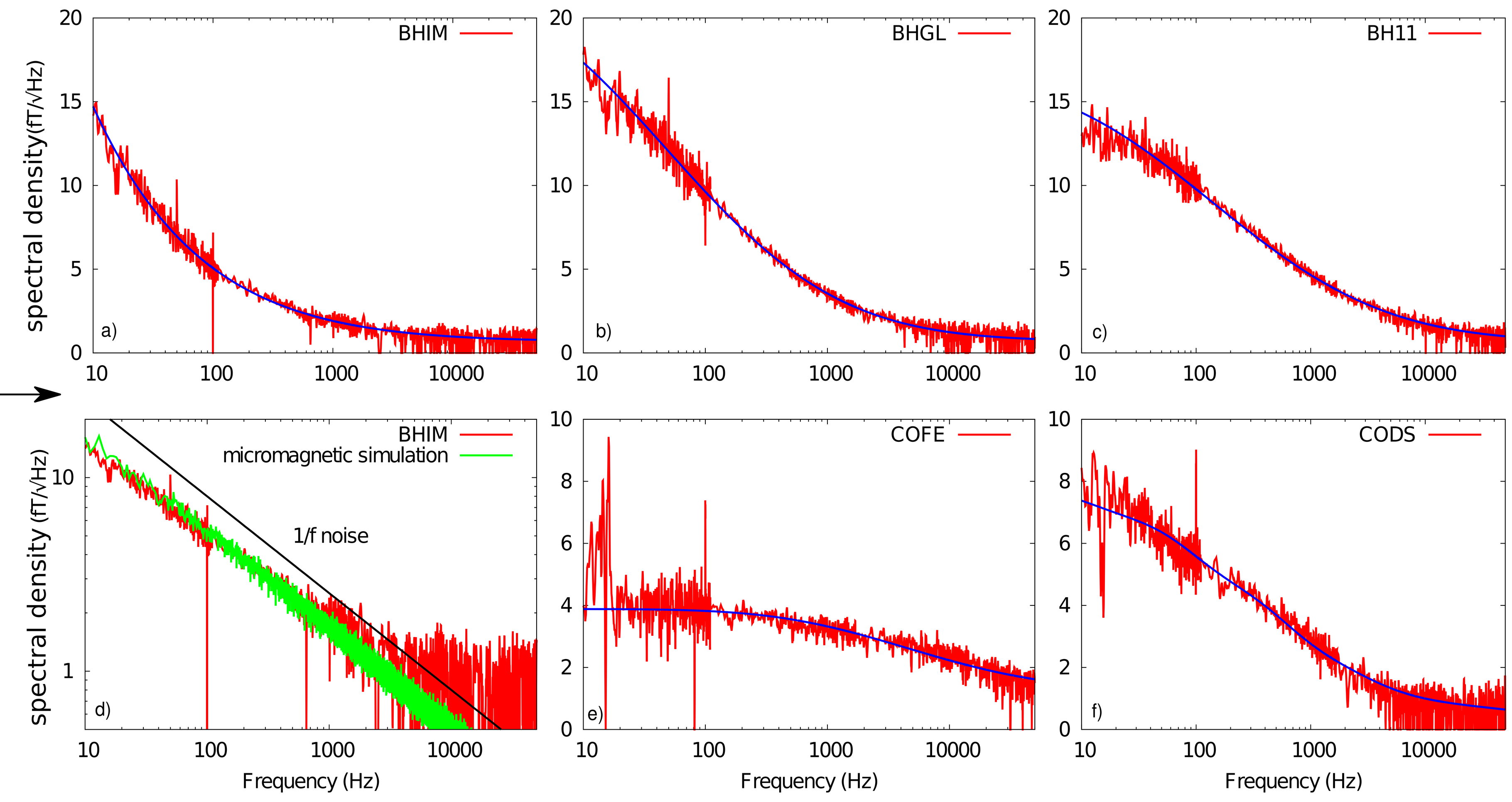
Normalized MRX measurement data (black crosses) for the different samples, together with the fitted relaxation curves (full lines).



The measured noise spectra togetherwith the background noise.

Results

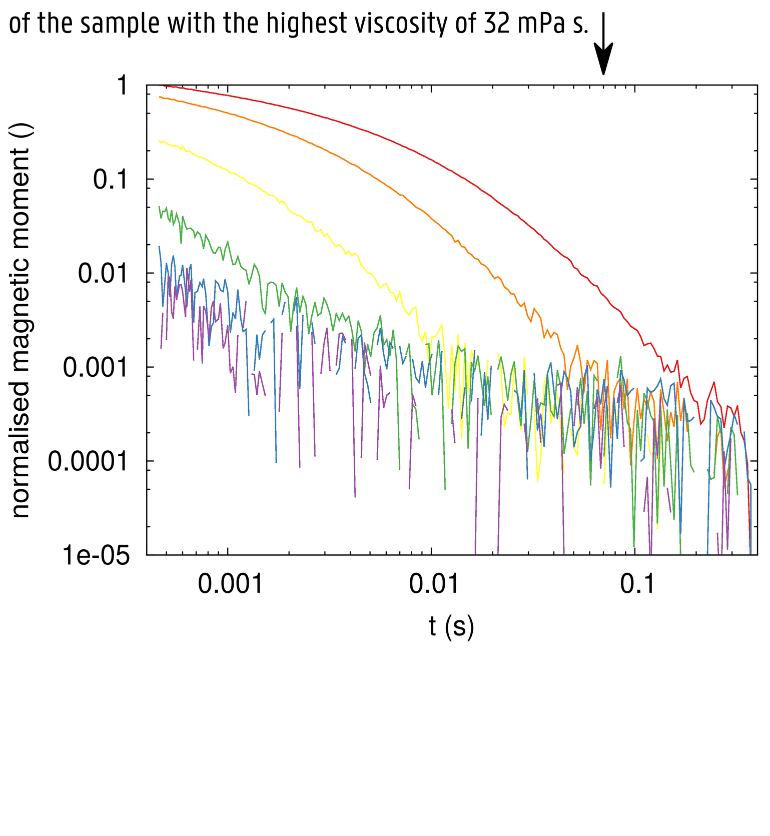
The **measured noise spectra** with the background noise quadratically subtracted (red lines). Below 1 fT/ Hz$^{1/2}$, the signal to noise ratio was too low to see a clear spectrum. The full blue lines correspond to the fitted spectrum. In contrast to the rest of the panels, panel (a) displays the noise spectrum with a linear y-axis. In panel (d), the spectrum of the BHIM sample is shown together with the spectrum generated with Vinamax (in green) and with a guide to the eye to illustrate the 1/f frequency dependence.

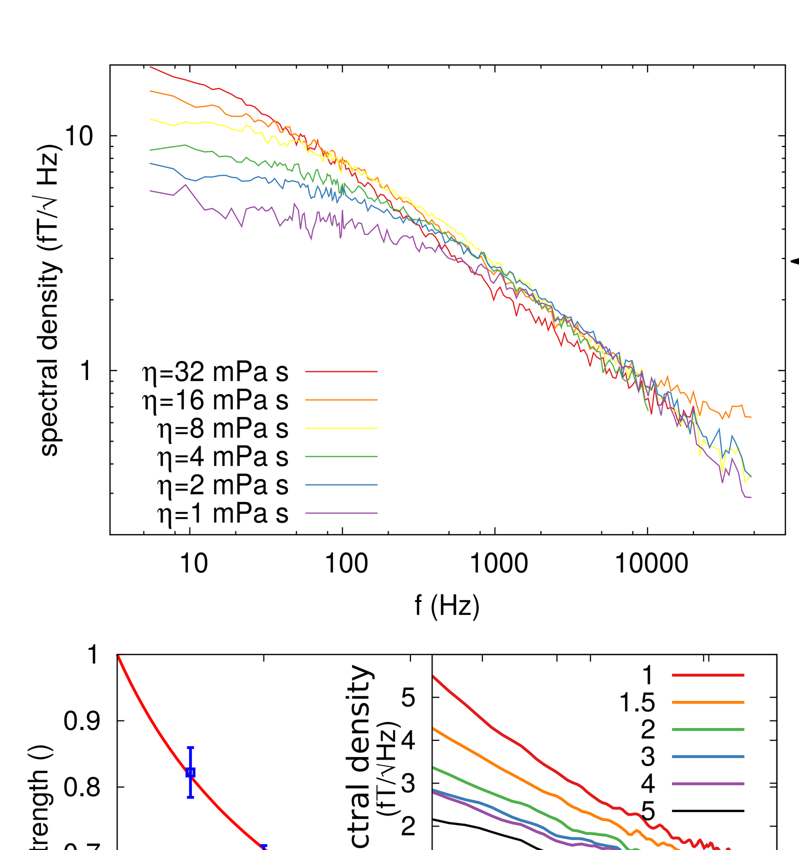


The parameters for the **hydrodynamic and core size distributions** of the different samples estimated from their MRX signal and their noise signal. μ has units of nm, the others are unitless. We used a saturation magnetization of 400 kA/m for all samples. The BH–samples were fitted with K = 11.5 kJ/m³ while the CO–samples were fitted with K = 100 kJ/ m³ , as determined from MRX-data. All liquid samples had a viscosity of 1 mPa s, except for the glycerol sample where we used a viscosity of 5.6 mPa s, in agreement with tabulated values. Here, $g(\nu) = \phi_N P(\nu_\mathrm{N}(V_\mathrm{c})) + (1-\phi_n) P(\nu_\mathrm{B}(V_\mathrm{h}))$

Sample	MRX μ_c	MRX σ_c	MRX μ_h	MRX σ_h	MRX ϕ_N	Noise spectrum μ_c	Noise spectrum σ_c	Noise spectrum μ_h	Noise spectrum σ_h	Noise spectrum ϕ_N
BHIM	18	0.15	–	–	1.00	21	0.13	–	–	1.00
BHGL	–	–	29	0.49	0.00	–	–	27	0.59	0.00
BH11	–	–	35	0.50	0.00	–	–	27	0.64	0.00
CODS	7.5	0.09	25	0.33	0.45	9.2	0.04	16	0.27	0.39
COFE	9.6	0.01	28	0.43	0.09	6.6	0.01	20	0.47	0.02

The relaxing magnetic moment, measured with MRX of a dilution series of Berlin Heart particles with several different viscosities. The background signal is subtracted and all relaxation curves are rescaled with the first value of the sample with the highest viscosity of 32 mPa s.



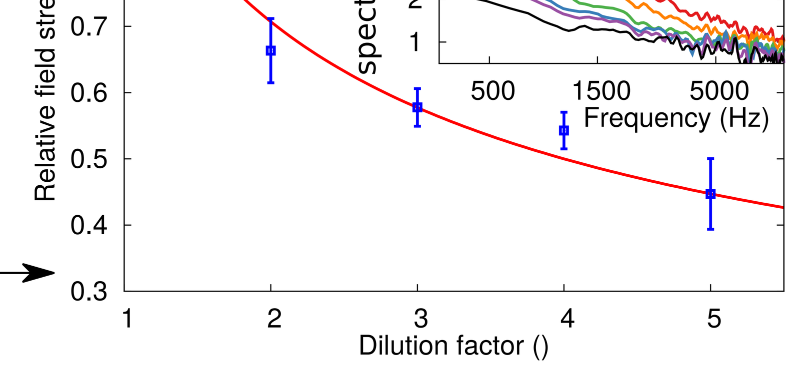


The TMNS of the same samples as the left figure with the background noise subtracted. For the lowest viscosities (4 mPa s), the MRX signal becomes very noisy, whereas the noise spectrum displays an acceptable signal to noise ratio over the entire spectrum for even the smallest viscosity, thus proving that TMNS has a **larger sensitivity towards smaller particles** than MRX.

Estimates of the **hydrodynamics size distributions** of a **second series of samples**. A "*" means that σ was kept fixed to this value and "–" indicates that the data was too noisy to be able to make a meaningful estimate.

Sample	TMNS μ (nm)	TMNS σ ()	MRX μ (nm)	MRX σ ()	η (mPa s)
BH	19.3	0.54*	-	-	1
	20.3	0.54*	-	-	2
	19.7	0.54*	10.2	0.54*	4
	17.8	0.54*	11.3	0.54*	8
	18.0	0.54*	17.1	0.54*	16
	20.6	0.54	20.7	0.54*	32
CFAS	42.2	0.34	-	-	1
	44.3	0.32	42.5	0.32	9.1
	63.3	0.17	40.2	0.35	32
CFHS	49.9	0.34	-	-	1
	48.2	0.32	50.1	0.29	12.2
	55.6	0.26	52.1	0.26	32

Finally, also a **dilution series** of Berlin Heart particles in water was investigated. The used dilution factors (DF) were 1 (undiluted), 1.5, 2, 3, 4, and 5 (corresponding to a 1 in 5 dilution). For these samples, we were only interested in the scaling of the noise amplitude. To this end, 5000 spectra between 100 and 12.9 kHz, logarithmically divided into 200 points, were averaged. **The spectral density scales with the square root of the dilution factor, as expected.**



Conclusions and Outlook

FEASIBILITY OF TMNS MEASUREMENTS AND INTERPRETATION

We **demonstrated the feasibility** to measure the magnetic noise spectrum of nanoparticle ensembles, of only a few (fT/ Hz$^{1/2}$), with SQUIDs in a magnetically shielded environment. A model was developed to interpret these noise spectra in terms of the relaxation rates of the paticles and their size distribution could be estimated. These **results were consistent with the size distributions obtained from other methods.**

ADVANTAGES

TMNS shows two **promising features to complement other characterization methods**
- it is able measure the nanoparticles in the absence of an external excitation. Whereas other methods measure the response to an external excitation **TMNS is an equilibrium measurement method**.
- increased **sensitivity towards smaller particles**.

OUTLOOK

- TMNS measurements might be used at different **offset fields** to investigate e.g. cluster formation.
- One can think of a **down-scaled device to quicky characterize nanoparticles** in a small lab environment

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